The Integrated Bio-Refinery:

Conversion of Corn Fiber to

Value-added Chemicals

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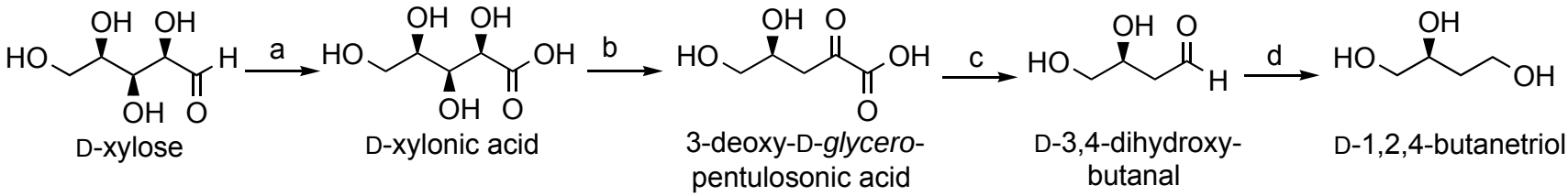
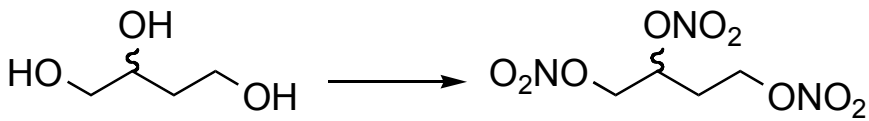
Key Topics

- Production of Chemicals from cellulose streams
  - Butanetriol from C5 sugars
  - Succinic acid from C5 or mixed sugars
- Succinic acid has the potential to replace important chemical intermediates
  - Demonstrated the ability to produce succinic acid and scaled the process to 1,000 gallon
  - Identified factors that will allow further cost reduction to better compete with commodity chemical feedstocks
  - Potential to integrate process with next generation dry mill ethanol plants

Green Production of Butanetriol BT





W. Niu, Molefe, M.N., and Frost, J. W. "Microbial Synthesis of the Energetic Material Precursor 1,2,4-Butanetriol" 2003, JACS *125*, 12998-12999.

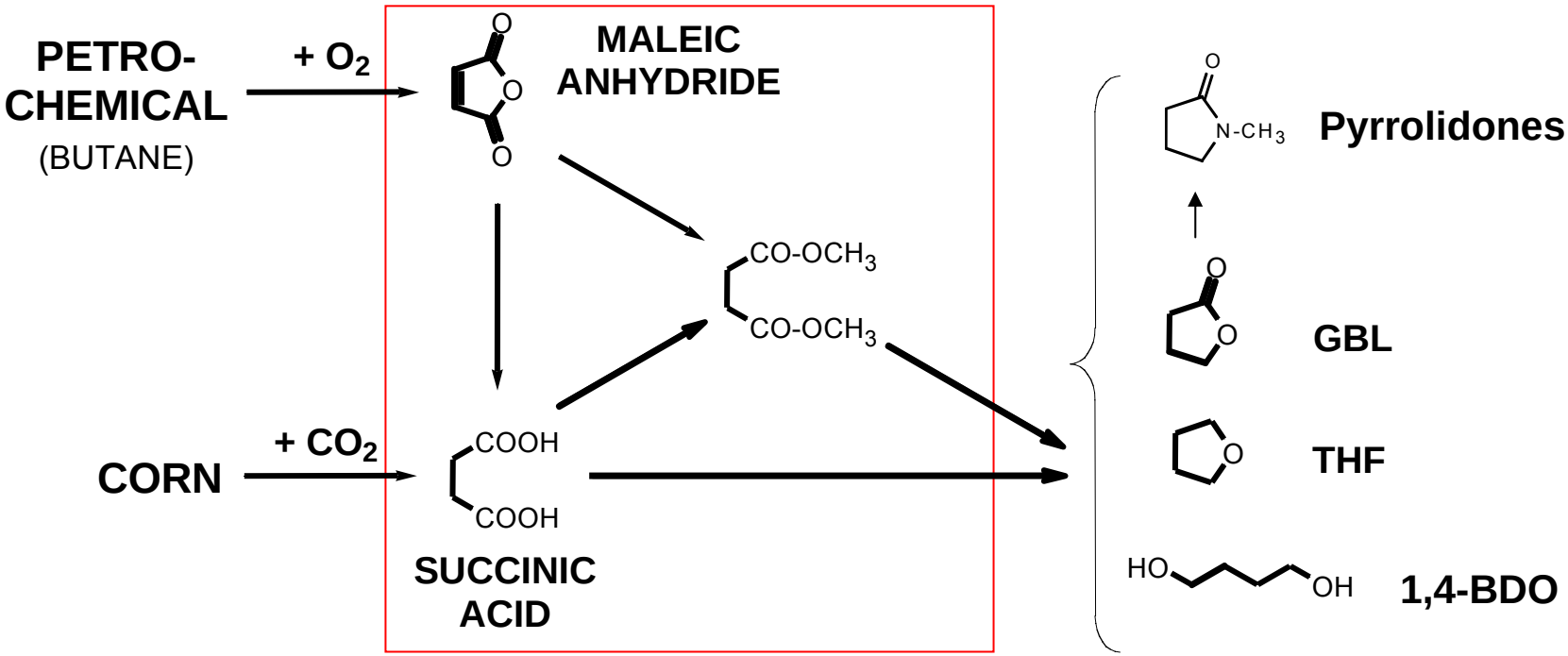
BTTN

- ***Advantage to NG***
  - Less volatile
  - Less shock sensitive
  - Lower freezing point
  - Thermally more stable

- ***Markets***
  - current: 15,000 lbs / year
  - Potential to increase to 180,000 Lbs /year

Succinic Acid:

Bioreplacement of Maleic Anhydride



Succinic Acid and succinate esters are current intermediates in various commercial routes from MA to GBL, THF, and BDO.

Succinic Acid:
Market

- ***Feedstock for Pyrrolidones***
  - Market Size: ~ 100 MM Lb/year
- ***Feedstock for Butanediol based Polymers***
  - Market Size: 1,636 MM Lbs/yr* (2004, ww)
  - Market size: 900 MM lbs/yr (2004, U.S.)
  - 4% estimated annual growth to 2015
  - polybutylene Terephthalate (PBT), and Thermoplastic Polyurethane (TPU)
- ***Replacement for Maleic Anhydride***
  - Market Size: 1.65 MM t/yr ** (2004, ww)
  - Tetrahydrofuran (THF), Butanediol (BDO), γ-butyrolactone (GBL)

** Chem. Market Reporter, 2005; Nexant Chem. Systems, 2004; ** China Chemical Reporter, 2005*

Succinic Acid Technology
Strain Development

- **Biocatalyst: *Actinobacillus succinogenes***
  - High Productivity
  - No product inhibition
  - High glucose tolerance
  - Facultative anaerobe
  - CO_2 incorporating
  - Utilizes broad range of sugars **simultaneously**

- **Improved Organism**
  - Reduced By-product formation through classic mutagenesis
  - Optimized yields through Metabolic Engineering

Succinic Acid Technology
Process Development

- **Fermentation**
  - Base neutralized batch Process
  - Utilization of low-value corn mill by-products as medium components

- **Recovery and Separation**
  - Cation Exchange
  - Carbon treatment
  - Crystallization
  - Yields a product of 98% purity

Biomass:
Inexpensive Sugar Source

- ***Starch:***

  Enzyme Hydrolysis → Glucose

- ***Cellulosics:***
  - Treatment required to release sugars
  - AFEX: Ammonia Fiber Expansion
    - Enhances enzyme access to cellulosic components
    - Developed by Dr. B. Dale, MSU
  - Enzyme Hydrolysis:
    - Releases sugars from starch and cellulose

Biomass: Corn Fiber

- ***Advantage***
  - Already collected material
    - corn wet mill by-product stream
    - corn fractionation based dry mills
- ***Treatments***
  - AFEX
  - Enzyme Hydrolysis → mostly C6 sugars → Ethanol
  - *Currently:* Dilute Acid treatment → C5 sugars → Succinic Acid

Corn Fiber
Sugar Streams

Endosperm C6 → Fermentative Ethanol Production → Ethanol + DDGS

Corn Fiber/ Bran → AFEX

AFEX → C6 → SSF → DDGS

SSF → Hydrolysis → *mostly* C5 → Fermentative Production

AFEX → Hydrolysis → C6 + C5 → Fermentative Production

Fermentative Production → Succinic Acid and/or 1,2,4-BT* + DDGS

Corn Fiber
Starch and Cellulose Products

79 % Endosperm → 50 MM gal Ethanol

11% Bran → Pre-Treatment

Pre-Treatment → SSF

Pre-Treatment → Hydrolysis

hemicellulose → Hydrolysis

Hydrolysis → C5 → Fermentation

Hydrolysis → C6 + C5 → Fermentation

SSF → 3.8 MM gal* Ethanol + 20 MM lbs Succinic *OR* 16 MM lbs BT

Fermentation → 75 MM lbs* Succinic (mixed sugars)

* Assumptions based on avg. size dry mill plant of ~16 MM bushels corn per year, yields based on theoretically achievable values

Summary
Succinic Fermentations

	Fraction of biomass derived sugars**			
	0%	15%	20%	25%
Succinic Titer [g / L]	50.7 ± 2.2	53.0	57.5	57.1
wt % -Yield* [g SA/g sugar]	72.0 ± 1.4	72.3	76.5	75.5

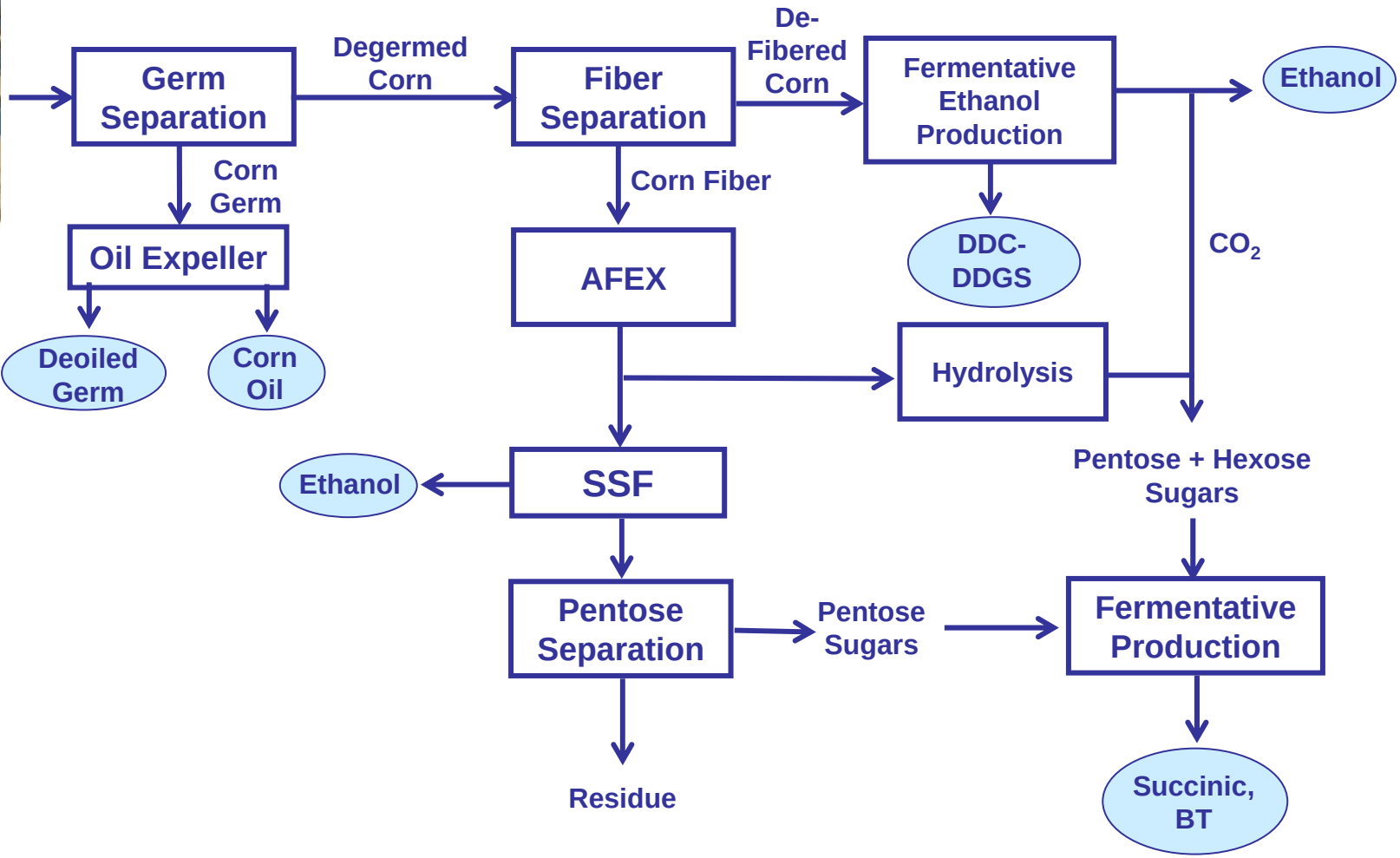
* Theoretical max. yields: 87% [g succinic / g C5 sugar]

** All fermentations started with xylose concentrations of ~ 70 g/L

Integration into Corn Milling

- Integration into future dry mills - feasible
  - Corn fractionation based dry mill
  - Use of single or mixed sugar streams from biomass (next generation application)
  - Succinic acid production is able to use CO_2 from ethanol production

Corn Fractionation based Dry Mill



Future Plans

- **Strain and process improvements for BT production**
- **Demonstrate succinic acid production with mixed sugar streams from additional biomass sources**
- **Improve product purity and develop recovery process with recycle stream**

Summary

- BT can be made via green production route
- Succinic acid has the potential to replace important chemical intermediates
- Demonstrated the ability to produce chemicals from hemicellulose streams
- Potential to reduce costs to better compete with commodity chemical feedstocks
  - Biomass as inexpensive carbon source
- Potential to integrate process for production of chemicals into next generation dry mill ethanol plants

Succinic Acid Team

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Thank You!